

Calorimetric study in single crystal of CsFe₂As₂

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We measured resistivity and specific heat of high-quality CsFe₂As₂ single crystals, which were grown by using a self-flux method. The CsFe₂As₂ crystal shows sharp superconducting transition at 1.8 K with the transition width of 0.1 K. The sharp superconducting transition and pronounced jump in specific heat indicate high quality of the crystals. Analysis on the superconducting-state specific heat supports unconventional pairing symmetry in CsFe₂As₂.

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I. INTRODUCTION

The discovery of iron-based superconductors has opened a new window for unveiling the physics of high-temperature superconductivity besides cuprates.¹⁻³ Among the various families of iron-based superconductors discovered till now, AFe₂As₂ (A=alkali earth, alkali, and Eu, the so called 122 system), which has the ThCr₂Si₂ structure, was the most investigated due to the easy growth of sizable high-quality single crystals.⁴ In this 122 system, KFe₂As₂, as the end member of the Ba_{1-x}K_xFe₂As₂ series, shows some unique properties. Firstly, superconductivity with $T_c \sim 4$ K can be realized in KFe₂As₂ without purposely doping. Secondly, very clean single crystal with residual resistivity ratio (RRR) exceeding 1000 can be quite easily achieved, which is a good start point to study intrinsic physical properties. It was proposed that inter-band interaction that links the hole and electron Fermi surfaces (FS) produces an s_{\pm} pairing symmetry in most of the iron-based superconductors. However, angle-resolved photoemission spectroscopy (ARPES) and the de Hass-van Alphen (dHvA) experiments revealed that the electron pockets disappeared and the large hole sheets centered around Γ point dominate FS in KFe₂As₂.^{7,8} Therefore, the pairing interaction could be distinct from other iron-based superconductors. The nodes on superconducting gaps have been detected by thermal conductivity,^{10,15} penetration depth,¹² and NMR.^{13,14} The measurements of thermal conductivity,^{15,16} specific heat¹⁷ and penetration depth¹² support a d -wave superconducting state in KFe₂As₂. In contrast, recent ultrahigh-resolution laser ARPES suggests a nodal s -wave superconductor with highly unusual FS-selective multi-gap structure.¹⁸ Whether those nodes are imposed by symmetry or accidental still remains an open question. As a consequence, further investigation on analogous compounds would be significant to clarify

the underlying physics in AFe₂As₂ system. In the present article, we will report the crystal growth and characterization of the analogous compound CsFe₂As₂.

Superconductivity at 2.6 K was observed in the polycrystalline CsFe₂As₂ sample.⁹ But few physical properties have been reported so far because high quality single crystals are not available until now. The difficulty of growing sizable CsFe₂As₂ single crystal mainly lies in the extremely high chemical activity and low melting point of Cs. In the present article, we have successfully overcome this problem by using the stainless steel sample container assembly,⁵ which can be sealed in the glove box (O₂ content is less than 1 ppm) mechanically. As a result, sizable high-quality single crystals of CsFe₂As₂ were grown. The CsFe₂As₂ single crystals were characterized by X-ray diffraction (XRD), resistivity, magnetic susceptibility, and specific heat. The sharp superconducting transition temperature and obvious specific jump indicate good quality of the single crystals.

II. EXPERIMENTAL DETAILS

High quality CsFe₂As₂ single crystals are grown by the self flux technique. The Cs chunks, Fe and As powder were weighted according to the ratio Cs:Fe:As=6:1:6. Typically, 1.5 grams of the mixture of Fe and As powders were loaded into a 10 mm diameter alumina crucible, and freshly cut Cs pieces were placed on top of the mixture. Then the alumina crucible with a lid was sealed in a stainless steel container assembly. The whole preparation process was carried out in the glove box in which high pure argon atmosphere is filled (O₂ content is less than 1 ppm). Considering the low melting point of Cs ($T_m=28$ °C), the room temperature must be kept below 20 °C. The sealed stainless steel assembly was then sealed inside an evacuated quartz tube. The quartz tube was placed in a box furnace and slowly heated up to 200 °C. It was kept at 200 °C for 400 minutes, which allows full reaction of Cs and the mixture. Then the sample was heated up to 950 °C in 10 hours. The temperature was kept still

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for 10 hours and then slowly cooled to 550 °C at a rate of 3 °C/h. After cooling down to room temperature by switching off the furnace, shiny plate-like crystals can be easily picked up from the alumina crucible. The single crystals are stable in air or alcohol for several days.

XRD was performed on a SmartLab-9 diffractometer(Rikagu) from 10° to 80° with a scanning rate of 4° per minute. The actual chemical composition of the single crystal is determined by energy dispersive x-ray spectroscopy(EDX) mounted on the field emission scanning electronic microscope (FESEM), Sirion 200. Magnetic susceptibility was measured using Vibrating Sample Magnetometer (VSM) (Quantum Design). The direct current (dc) resistivity was measured by conventional four probe method using the PPMS-9T (Quantum Design). Resistivity and specific heat down to 50 mK were measured in a dilution refrigerator on PPMS.

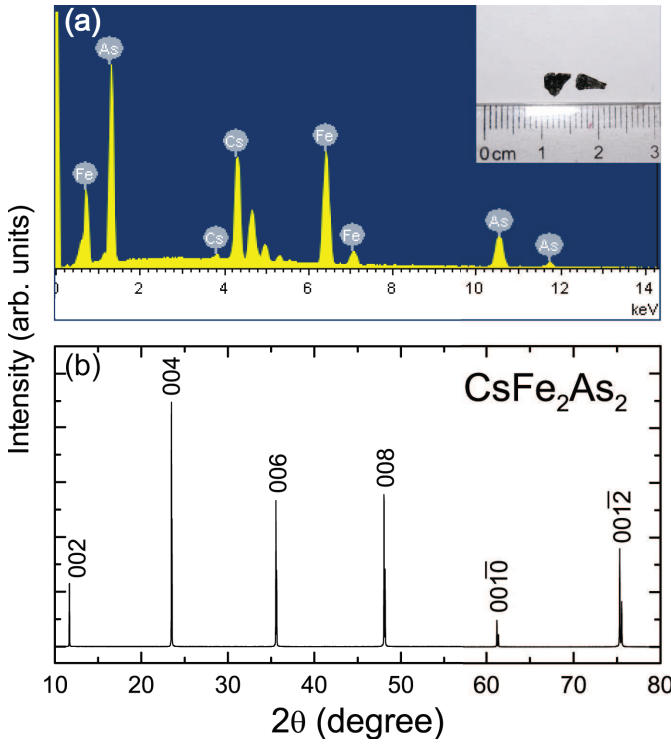


FIG. 1: (color online). (a) The typical EDX spectrum for CsFe₂As₂ single crystal, the inset shows photograph of the CsFe₂As₂ single crystal together with a millimeter scale. (b) X-ray diffraction pattern of the CsFe₂As₂ single crystal.

III. RESULTS

The typical size of as grown single crystals is about 5 mm × 3 mm × 0.03 mm, as shown in the inset of Fig. 1(a). Elemental analysis was performed using EDX. A typical EDX spectrum is shown in Fig.1(a), and the obtained atomic ratio of Cs:Fe:As is roughly 20.76: 40.52: 38.71. The atomic ratio is consistent with the composi-

tion CsFe₂As₂ within instrumental error. Fig.1(b) shows the single crystal XRD pattern for CsFe₂As₂. Only (00 l) reflections can be recognized, indicating that the crystal is well orientated along the c axis. The c -axis lattice parameter was estimated to be $c=15.13$ Å, consistent with previous report on the polycrystalline samples.⁹

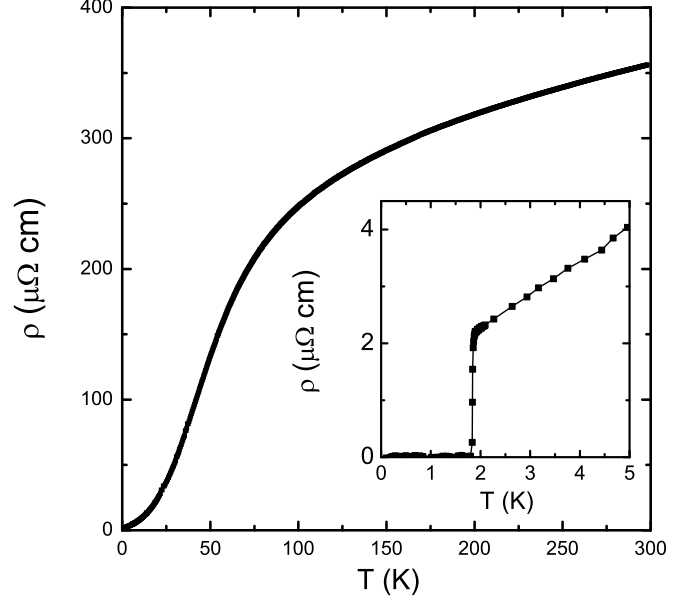


FIG. 2: (color online). Resistivity plotted as a function of temperature for CsFe₂As₂ single crystal. The inset is the zoom plot of resistivity around the superconducting transition.

Fig. 2 shows the in-plane resistivity as the function of the temperature for CsFe₂As₂ single crystal. The resistivity exhibits metallic behavior in the entire temperature range between 60 mK to 300 K. The behavior of the resistivity resembles the counterpart compound KFe₂As₂. The resistivity begins to drop rapidly at 1.88 K and reaches zero at 1.8 K. The superconducting transition temperature T_c in the following text is defined as the temperature when the resistivity reaches zero. The sharp superconducting transition with transition width less than 0.1 K indicates high quality of the crystal. The T_c of CsFe₂As₂ is slightly lower than that reported on the polycrystalline sample.⁹ The residual resistivity ratio (RRR) $\rho(300\text{K})/\rho(5\text{K})$ is estimated to be 88, comparable with those in the crystals of KFe₂As₂ grown with FeAs flux,^{10,11} but much smaller than those in crystals of KFe₂As₂ grown with KAs.^{5,16}

Fig. 3 shows the the temperature dependence of the in-plane magnetic susceptibility for CsFe₂As₂ single crystal under $H = 1$ T in the normal state. The CsFe₂As₂ single crystal shows paramagnetic behavior from 300 K to 2 K, and no magnetic anomaly was observed. The magnetic susceptibility behavior of CsFe₂As₂ is similar to KFe₂As₂.²²

In Fig. 4(a), we show the temperature dependence of the specific heat of CsFe₂As₂ down to 50 mK under zero

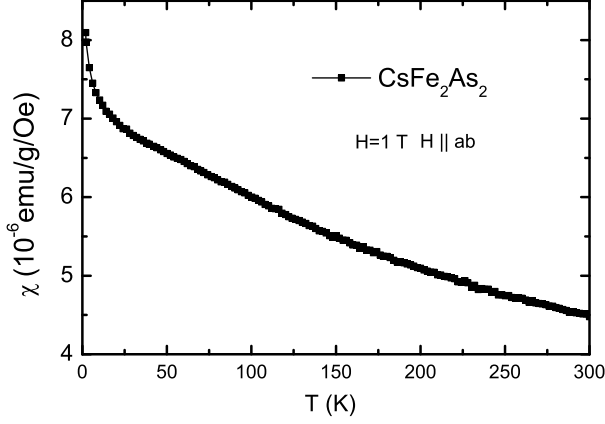


FIG. 3: (color online). Temperature dependence of magnetic susceptibility of the CsFe₂As₂ single crystal collected at $H=1$ T with $H \parallel ab$.

magnetic field. A pronounced jump due to the superconducting transition is observed below 1.8 K, consistent with the resistivity measurement. This indicates the high quality of the present crystals. The normal-state specific heat can be well fitted by $C_{\text{normal}}(T) = \gamma_N T + C_{\text{lattice}}(T)$, where $\gamma_N T$ and $C_{\text{lattice}}(T) = \beta T^3 + \eta T^5$ are electron and phonon contributions, respectively.²⁵ The solid line in Fig. 4(a) is the best fit to the C_p/T above T_c (1.9 K to 10 K). We obtained $\gamma_N = 184.01 \text{ mJ mol}^{-1} \text{ K}^{-2}$, $\beta = 0.466 \text{ mJ mol}^{-1} \text{ K}^{-4}$ and $\eta = 0.00474 \text{ mJ mol}^{-1} \text{ K}^{-6}$. From this value of β and by using the formula $\Theta_D = [12\pi^4 k_B N_A Z / (5\beta)]^{1/3}$, where N_A is the Avogadro constant and Z is the total number of atoms in one unit cell, the Debye temperature (Θ_D) is estimated to be 275 K. This value is comparable to that of KFe₂As₂.²⁰ It should be pointed out that $\gamma_N = 184.01 \text{ mJ mol}^{-1} \text{ K}^{-2}$ is very large. The specific heat jump is only about 31% of γ_N , which is similar to the case of KFe₂As₂.^{13,17,20,22} Considering the sharp superconducting transition, this feature may be the evidence for the existence of low energy quasiparticle excitation.¹³ $\Delta C_p / \gamma T_c$ can be estimated to be about 0.35. This is much smaller than the value ($=1.43$) expected for BCS superconductors, which could indicate an unconventional pairing symmetry. In addition, $\Delta C_p / T_c$ at $T_c = 1.8 \text{ K}$ is estimated to be about $64 \text{ mJ mol}^{-1} \text{ K}^{-2}$, far above the $\Delta C_p / T_c$ vs. T_c behavior of other iron-based superconductors, except for that observed in KFe₂As₂. In KFe₂As₂, $\Delta C_p / T_c \approx 41 \text{ mJ mol}^{-1} \text{ K}^{-2}$ at $T_c = 3.1 \text{ K}$,²¹ which is also much above the $\Delta C_p / T_c$ vs. T_c behavior of other iron-based superconductors. This suggests that the pairing symmetry in CsFe₂As₂ could be similar to that in KFe₂As₂, but different from that of other iron-based superconductors.

Fig. 4(b) shows the superconducting electronic specific heat difference between the superconducting and normal states $\Delta C_p(T) = C_{\text{es}} - \gamma_N T = C_p(T) - C_{\text{normal}}(T)$, for which the entropy conservation is confirmed to

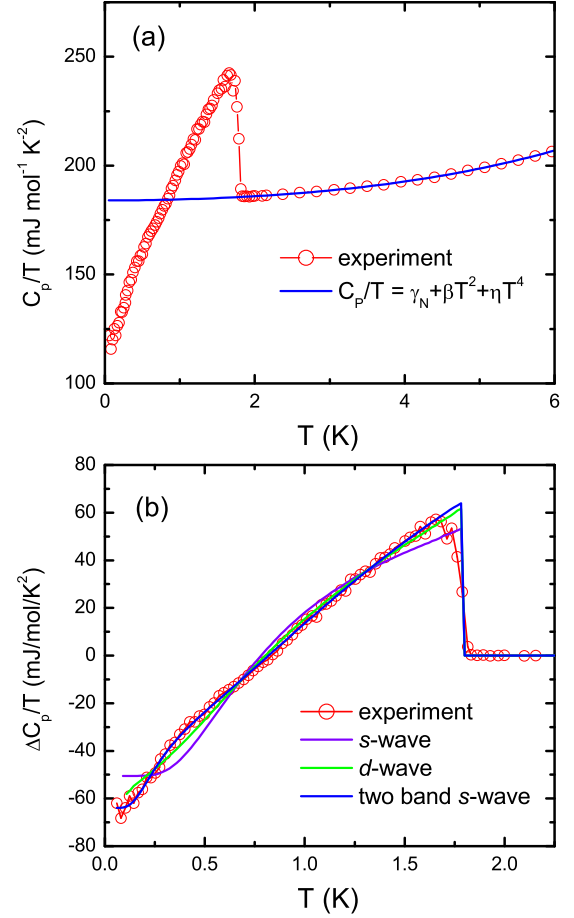


FIG. 4: (color online). (a) Temperature dependence of specific heat divided by temperature $C_p(T)/T$ of CsFe₂As₂. The blue solid line is the fitting for the data between 1.9 and 10 K (data below 6 K are shown). The fitting function is described in the text. (b) Temperature dependence of the difference in the electronic specific heat between the superconducting state and the normal state. The violet, green and blue solid line represent fits for the experimental data by using single band s -wave ($\alpha = 1.42$), single band d -wave ($\alpha = 1.93$) and two band s -wave α model ($\alpha_1 = 1.21$, $\alpha_2 = 3.33$), respectively.

be satisfied. In the low-temperature limit, the s -wave model predicts $\Delta C/T \cong aT^{-5/2} \exp(-\Delta/k_B T) - \gamma_n$. While in clean d -wave model, $C_{\text{es}} \sim T^2$, which gives $\Delta C_p/T = \alpha T - \gamma_n$, as have been observed in organic superconductors κ -(BEDT-TTF)₂Cu[N(CN)₂]Br and κ -(BEDT-TTF)₂Cu(NCS)₂.²³ Fig. 4(b) indicates that $\Delta C_p/T$ can't be described by a single-band BCS α -model with $\alpha = \Delta(0)/k_B T_c = 1.42$.²⁴ As a consequence, our results exclude the single-band s -wave pairing symmetry. As shown in Fig. 4(b), single-band d -wave and two-band s -wave model give rise to better fitting quality.^{25,26} The low-temperature part of the specific heat roughly follows linear temperature dependence rather than exponent, so the gap symmetry is likely d -wave. The thermal conductivity measured on the same batch of

CsFe₂As₂ single crystals indicates nodal superconducting gap symmetry.²⁷ It has been reported that there is an anomaly around 0.7 K in C_p/T of KFe₂As₂, which was thought to be related to the impurity contribution in the sample,⁶ and higher quality of crystals can almost eliminate such anomaly.¹⁷ A very weak anomaly-like feature is observed below 0.55 K in our data too, which may affect the result of the fit. This makes it hard to make sure the pairing symmetry from our fittings, since the main difference between the fitting in d -wave and two-band s -wave models lies below 0.55 K. Further measurements, such as ARPES and NMR, should be performed to illustrate the pairing symmetry.

IV. SUMMARY AND CONCLUSIONS

We have successfully grown CsFe₂As₂ single crystals using the assembly of stainless steel container. The sharp drop in resistivity and pronounced jump in specific heat

with T_c around 1.8 K indicate the high quality of crystals. The behavior of resistivity, magnetic susceptibility, and specific data resemble the counterpart compound KFe₂As₂. The T dependence of the specific heat in the superconducting state may be explained by a d -wave or a multi-band s -wave superconducting gap pictures. More work is required to reach a consensus for the pairing symmetry in this system.

Acknowledgements

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